REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
07-02-2016	Final Report	15-Nov-2014 - 14-Aug-2015

4. TITLE AND SUBTITLE	
Final Report: Conductivity Dynamics of the Metal to Insulator Transition in EuNiO3/LANiO3 Superlattices	5a. CONTRACT NUMBER W911NF-14-1-0643
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER 611102
6. AUTHORS Richard D. Averitt	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES	8. PERFORMING ORGANIZATION REPORT NUMBER
University of California - San Diego 9500 Gilman Drive Mailcode 0934 La Jolla, CA 92093 -0934	

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)	10. SPONSOR/MONITOR'S ACRONYM(S) ARO
U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211	11. SPONSOR/MONITOR'S REPORT NUMBER(S) 66407-PH-II.1

12. DISTRIBUTION AVAILIBILITY STATEMENT

Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

In numerous transition metal oxides (TMO), competition between the charge, lattice, spin, and orbital degrees of freedom lead to emergent phenomena with the insulator-to-insulator transition (IMT) being one of the most enigmatic from fundamental and applied perspectives. Recently, considerable effort has focused on the growth of TMO heterostructures with atomic layer precision with a view towards controlling and even creating new emergent behavior including the IMT. Simultaneously, ultrafast optical spectroscopy (UOS) has become a powerful approach

15. SUBJECT TERMS

Ultrafast Optical Spectroscopy, Terahertz Spectroscopy, Nickelate, Superlattice

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
UU	UU	UU	UU		RICHARD AVERITT
					19b. TELEPHONE NUMBER 858-534-5976

Standard Form 298 (Rev 8/98)
Prescribed by ANSI Std. Z39.18

Report Title

Final Report: Conductivity Dynamics of the Metal to Insulator Transition in EuNiO3/LANiO3 Superlattices

ABSTRACT

In numerous transition metal oxides (TMO), competition between the charge, lattice, spin, and orbital degrees of freedom lead to emergent phenomena with the insulator-to-insulator transition (IMT) being one of the most enigmatic from fundamental and applied perspectives. Recently, considerable effort has focused on the growth of TMO heterostructures with atomic layer precision with a view towards controlling and even creating new emergent behavior including the IMT. Simultaneously, ultrafast optical spectroscopy (UOS) has become a powerful approach to interrogate emergence, probing how interactions and competition between operative degrees of freedom in TMOs determine macroscopic properties. In this STIR project an initial foray into non-equilibrium studies in nickelate superlattices was pursued to investigate IMT dynamics. Using time-resolved terahertz spectroscopy we measured the non-equilibrium recovery of the initial low-temperature antiferromagnetic insulating phase following a picosecond quench to the high temperature paramagnetic metallic phase. Following photo-excitation, the recovery proceeds through nucleation and growth of the AFI phase at the expense of the PM phase following rapid cooling below the IMT transition temperature (~150K). These results highlight the importance of mesoscopic physics in correlated materials revealing new length and timescales that arise during the course of a phase transition.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. R.D. Averitt, "Conductivity Dynamics of the Metal-to-Insulator Transition in Nickelate Superlattices," invited talk at 8th International Conference on Materials for Advanced Technologies, Symposium I, Optical Properties of Two-Dimensional Heterostructures from THz to X-ray July 3rd, 2015, Singapore.

2. Thorsmolle VK, Zhang J, Middey S, Abreu E, Zhang G, Post KW, Basov D, Chakhalian J, Averitt RD, “Conductivity Dynamics of the Metal-to-Insulator Transition in EuNiO3/LaNiO3 Superlattices,” poster presented at Big Ideas Conference on Quantum Materials, La Jolla CA, Dec. 14-17, 2015.

2. Thorsmolle VK, Zhang J, Middey S, Abreu E, Zhang G, Post KW, Basov D, Chakhalian J, Averitt RD, “Conductivity Dynamics of the Metal-to-Insulator Transition in EuNiO3/LaNiO3 Superlattices,” poster to be present Gordon Research Conference on Ultrafast Phenomena in Cooperative Systems, February 14 - 19, Lucca Italy.

Number of Presentations: 3.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Gufeng Zhang	0.50	
Peter Kissin	0.50	
FTE Equivalent:	**1.00**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Richard Averitt	0.05	
FTE Equivalent:	**0.05**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

Abstract:

In numerous transition metal oxides (TMO), competition between the charge, lattice, spin, and orbital degrees of freedom lead to emergent phenomena with the insulator-to-insulator transition (IMT) being one of the most enigmatic from fundamental and applied perspectives. Recently, considerable effort has focused on the growth of TMO heterostructures with atomic layer precision with a view towards controlling and even creating new emergent behavior including the IMT. Simultaneously, ultrafast optical spectroscopy (UOS) has become a powerful approach to interrogate emergence, probing how interactions and competition between operative degrees of freedom in TMOs determine macroscopic properties. In this STIR project an initial foray into non-equilibrium studies in nickelate superlattices was pursued to investigate IMT dynamics. Using time-resolved terahertz spectroscopy we measured the non-equilibrium recovery of the initial low-temperature antiferromagnetic insulating phase following a picosecond quench to the high temperature paramagnetic metallic phase. Following photo-excitation, the recovery proceeds through nucleation and growth of the AFI phase at the expense of the PM phase following rapid cooling below the IMT transition temperature (~150K). These results highlight the importance of mesoscopic physics in correlated materials revealing new length and timescales that arise during the course of a phase transition.

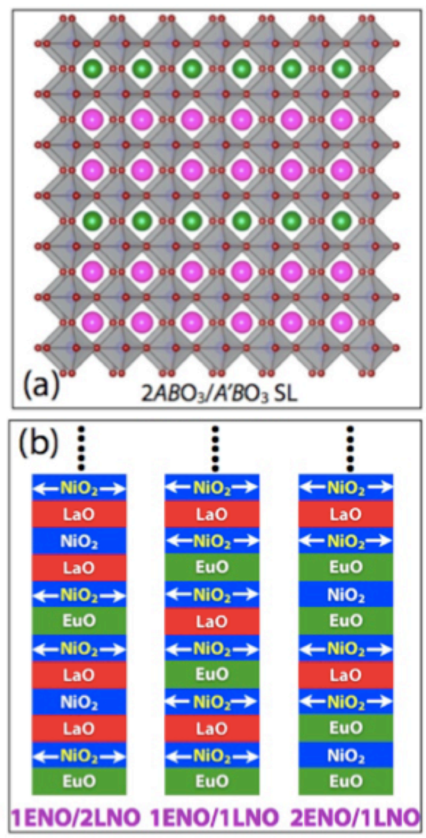

Figure 1: (a) Schematic of perovskite SL structure with 2:1 RE repeat sequence. (b) Example repeat sequences for ENO/LNO superlattices.

Statement of Problem Investigated: Complexity in transition metal oxides can be understood as a delicate balance between competing interactions, which gives rise to an energy landscape whose details are not easily discerned [1]. An increasingly successful approach to tackle this problem is that of time resolved experiments, where the fundamental timescales of the system properties can be investigated through their response to appropriately chosen femtosecond photoexcitation [2,3].

Ultrafast optical studies of the insulator-to-metal transition (IMT) are of particular interest as there are interesting fundamental questions beyond trying to disentangle the microscopic origin of the IMT in a given material. What are the timescales of the IMT? Can photoexcitation effectively collapse the Mott-Hubbard gap? Are there multiple unique pathways to (e.g. mode selective excitation – see [2] [3]) to drive the IM transition? Can the metallic state be reversibly controlled with photoexcitation? Do mesoscale phenomena (e.g. phase separation) influence the dynamics of the IMT? Does symmetry play a determining role during the course of a non-equilibrium IMT? Some insight into these questions

has been obtained in studies of the vanadates, with most of the work being on VO_2 [4-10]. VO_2 exhibits a transition from a monoclinic insulator to a rutile metal at ~340K. Ultrafast studies indicate that, following optical excitation, a finite density of state appears at the Fermi level in approximately ~1ps. This transient state appears to correspond to an intermediate monoclinic metallic state en route to the full metallic phase, which is obtained on a longer timescale (~100ps) through nucleation and growth of the rutile structure. Thus, it appears that there are multiple length and timescales along with non-equilibrium intermediate states associated with the dynamic IMT in VO_2.

To address the aforementioned fundamental questions, it is necessary to investigate IMT dynamics in other materials. The perovskite nickelates (RE)NiO_3 have emerged as an important class of IMT materials, exhibiting rich IMT phenomena across the rare earth (RE) series that includes La, Pr, Nd, Sm, Eu, Y, and Lu [11,12]. Quite recently, growth of digital nickelate superlattices (SL) has been achieved (Prof. Jak Chakhalian, University of Arkansas), offering a route to control the IMT by varying the relative number of subunits comprising the superlattice (Figure 1(a)). In particular, SL comprised of $EuNiO_3$ (ENO) and $LaNiO_3$ (LNO) enable tuning of the IMT by varying the relative number ENO/LNO layers as shown in Figure 1(b). Importantly, ENO/LNO superlattices range from robust metal exhibiting no IMT (pure LNO) to insulator (ENO) in a quasi-continuous fashion with a clear evolution from a first-order to near second-order IMT upon increasing the relative number of ENO layers in comparison to LNO. This is accomplished without the need for multiple substrates (i.e. different strain states) simplifying ultrafast experiments and providing a unique level of control, making ENO/LNO superlattices of extreme interest to investigate IMT dynamics.

The objective of this STIR proposal was to investigate photo-initiated insulator to metal transition dynamics in ENO/LNO superlattices. In this project we utilized optical-pump terahertz-probe spectroscopy (OPTP) to measure a series of ENO/LNO SL where the relative number of ENO and LNO units is controlled through epitaxial growth.

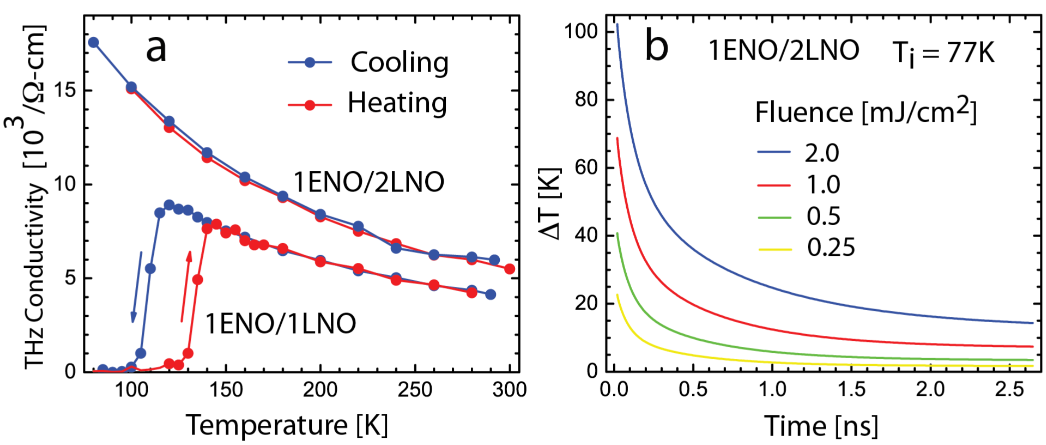

Figure 2: a) THz conductivity as a function of temperature for 1ENO/2LNO and 1ENO/1LNO superlattices. b) Experimentally determined temperature in 1ENO/2LNO superlattice as a function of time at various incident fluences for an initial temperature of 77K.

Summary of Main Results: An initial foray into non-equilibrium studies in heterostructures was enabled this STIR to investigate the dynamics of the insulator-to-metal transition (IMT) in nickelate superlattices (SL) [13].

Figure 2a plots the THz conductivity (not photoexcited) as a function of temperature for 1ENO/2LNO and 1ENO/1LNO superlattices. The samples have a thickness of 36 unit cells (~15nm) and are grown on $NdGaO_3$ (NGO). While 1ENO/1LNO exhibits a first order IMT, 1ENO/2LNO does not exhibit a phase transition, instead exhibiting a monotonic decrease in conductivity with increasing temperature. As such, the single exponential dynamics (not shown) observed in optical-pump THz-probe studies of 1ENO/2LNO provide the means to quantitatively track the temperature in these ultrathin films. This is shown in Fig. 2b, which plots the evolution of the temperature (after electron-phonon equilibration in ~1ps) as a function of time at various incident fluences for an initial temperature of 77K. The cooling in these films is quite rapid. Given the similarity in the lattice structure and thermal properties of 1ENO/1LNO and 1ENO/2LNO, the results of Fig. 2b can be utilized to obtain an accurate estimate of the temperature in the 1ENO/1LNO films that exhibit an IMT. This was crucial to obtaining an understanding of the IMT dynamics presented in Figure 3.

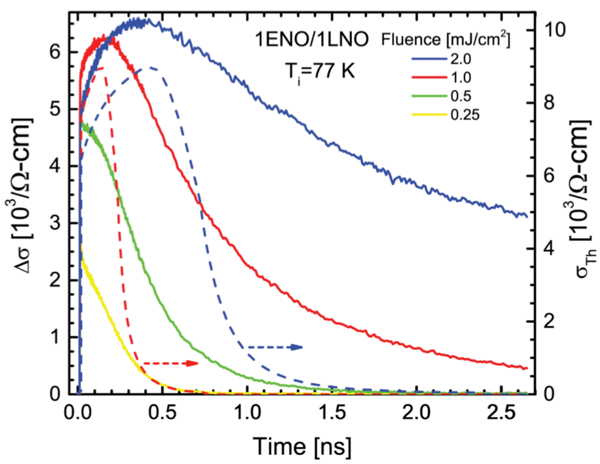

Figure 3: Photoinduced conductivity dynamics in 1ENO/1LNO SL as a function of time at various fluences. The AFI→PM transition occurs in ~1ps, with a non-thermal recovery exhibiting a marked fluence dependence. This recovery corresponds to PM→AFI recovery, which proceeds after rapid cooling by growth of the AF phase into the PM phase, which is by definition a non-equilibrium process. Measurements of a 1ENO/2LNO superlattice (which doesn't have an IMT) serve as a precise experimental thermometer, allowing for the construction of recovery curves (dashed lines) assuming a pure thermal relaxation. The dashed lines show the actual data (solid lines) deviate strongly from a thermal recovery.

We performed optical-pump THz-probe studies of the conductivity dynamics in 1ENO/1LNO SL, which exhibits a first order IMT at 130K from a low-temperature antiferromagnetic insulating (AFI) phase to a high-temperature paramagnetic metallic (PM) phase. We identified, as shown in Figure 3, non-equilibrium recovery of the AFI phase following a picosecond quench to the high temperature PM phase. There is a strong fluence dependence of the recovery of the AFI ground state. The recovery proceeds through nucleation and growth of the AFI phase into the PM phase following rapid cooling below T_c (cooling determined from measurements on 1ENO/2LNO SL as described above). In particular, the dashed lines in Fig. 3 plot the expected recovery dynamics if the conductivity recovery was solely determined by the local temperature. Clearly, the experimental recovery plotted as solid lines (color coded to match the dashed lines for a give fluence) exhibits a delayed recovery. The recovery is nonthermal and corresponds to nucleation and growth of the AFI phase once the sample has supercooled to below T_c. The observed first order kinetics can be described by the Avrami equation for nucleation and growth [14,15]. Importantly, without the temporal evolution of the temperature

obtained from the 1ENO/2LNO dynamics, it would not have been possible to obtain this level of insight into the 1ENO/1LNO IMT recovery dynamics.

The dynamics in the 1ENO/1LNO SLs are in marked contrast to the vanadates. For the 1ENO/1LNO sample it is observed that upon photoexcitation there is a prompt collapse of the antiferromagnetic insulating (AFI) to the paramagnetic metallic phase (PM) in ~1ps. In contrast, this takes 10's of picoseconds in the vanadates. Additionally, the conductivity change is larger and requires a considerably lower fluence in comparison to the vanadates. The continued increase in the conductivity in Figure 3 (especially evident in the higher fluence curves – e.g. the blue solid line) arises from cooling while still in the PM phase (e.g. see the slope the conductivity of the 1ENO/1ENO curve above T_c in Fig. 2a). At the peak of the conductivity curve, the sample has cooled to T_c at which point a recovery of the insulating phase starts. The recovery, while longer than expected for pure thermal relaxation, is quite rapid in comparison to the vanadates. This is an interesting point for potential IMT switching application and is likely related (in part) to the minor structural changes in the nickelates across the IMT in comparison to the vanadates. In summary, our initial investigation of nickelate superlattices has revealed novel IMT dynamics associated with nucleation and growth associated with the first order phase transition dynamics. Future studies will focus of the dynamics of the lattice and magnetic degrees of freedom during the course of the transition.

Bibliography:

[1] Rondinelli JM, May SJ, Freeland JW, "Control of octahedral connectivity in perovskite oxide heterostructures: an emerging route to multifunctional materials discovery," *MRS Bull.* 37, 261 (2012).

[2] Orenstein J, "Ultrafast spectroscopy of quantum materials," *Phys. Today* 65, 44 (2012).

[3] Zhang J, Averitt RD, "Dynamics and control in transition metal oxides," Ann. Rev. Mat. Res. 44, (2014). DOI: 10.1146/annurev-matsci-070813-113258.

[4] Cavalleri A, Rini M, Chong H, Fourmaux S, Glover T, et al., "Band-selective measurements of electron dynamics in VO_2 using femtosecond near-edge X-ray absorption," *Phys. Rev. Lett.* 95, 067405 (2005).

[5] Kübler C, Ehrke H, Huber R, Lopez R, Halabica A, et al., "Coherent structural dynamics and electronic correlations during an ultrafast insulator-to-metal phase transition in VO_2," *Phys. Rev. Lett.* 99, 116401 (2007).

[6] Pashkin A, Kübler C, Ehrke H, Lopez R, Halabica A, et al. 2011. Ultrafast insulator-metal phase transition in VO_2 studied by multiterahertz spectroscopy. *Phys. Rev. B* 83(19):195120.

[7] Hilton D, Prasankumar R, Fourmaux S, Cavalleri A, Brassard D, et al., " Enhanced photosusceptibility near T_c for the light-induced insulator-to-metal phase transition in vanadium dioxide," *Phys. Rev. Lett.* 99, 226401 (2007).

[8] Liu M, Hwang HY, Tao H, Strikwerda AC, Fan K, et al., "Terahertz-field-induced insulator-to-metal transition in vanadium dioxide metamaterial," *Nature* 487, 345 (2012).

[9] Cavalleri A, Dekorsy T, Chong H, Kieffer J, Schoenlein R, "Evidence for a structurally-driven insulator-to-metal transition in VO_2: a view from the ultrafast timescale," *Phys. Rev. B* 70, 161102 (2004).

[10] Rini M, Cavalleri A, Schoenlein RW, López R, Feldman LC, et al., "Photoinduced phase transition in VO_2 nanocrystals: ultrafast control of surface-plasmon resonance," *Opt. Lett.* 30, 558 (2005).
[11]Medarde ML, "Structural, magnetic and electronic properties of $RNiO_3$ perovskites (R = rare earth)," *Journal of Physics: Condensed Matter* 9, 1679 (1997).
[12] Catalan G, "Progress in perovskite nickelate research," *Phase Transitions* 81, 729 (2008).
[13] Thorsmolle VK, Zhang J, Middey S, Abreu E, Zhang G, Post KW, Basov D, Chakhalian J, Averitt RD, "Conductivity Dynamics of the Metal-to-Insulator Transition in $EuNiO_3/LaNiO_3$ Superlattices," to be submitted.
[14] Abreu, E, Wang S, Ramirez JG, Liu M, Zhang J, Geng K, Schuller IK, Averitt RD, "Dynamic conductivity scaling in photoexcited V_2O_3 thin films," Phys. Rev. B. 92 085130, (2015).
[15] Fanfoni, M. & Tomellini, M. T"he Johnson-Mehl- Avrami-Kohnogorov model: A brief review," *Nuovo Cim. D* 20**,** 1171 (1998).